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Pair- and many-atom interactions in the cohesion of surface clusters: Pd_x and Ir_x on W(110)

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In order to explore cohesion in surface clusters, interactions between Pd atoms adsorbed on W(110) have been characterized in observations of individual adatoms using a helium-cooled field ion microscope. The free energies of pair interactions $F(\mathbf{R})$ have been derived from detailed measurements of the probability of finding two atoms on an otherwise empty plane at a vector separation $\mathbf{R}$ from each other. For Pd, pair free energies are similar to previous results for Ir atoms: interactions extend over distances larger than 13 Å, and show a strong directional anisotropy. Along the close-packed $[1\bar{1}\bar{1}]$ direction, interactions between two Pd atoms are very close to those for Ir adatoms, even though the binding energy of Ir atoms to the substrate is more than twice that of Pd. With quantitative pair free energies available, the contributions from many-atom effects to the cohesion of clusters have been evaluated by examining the transformation from chain structures to two-dimensional islands, which takes place with both Pd and Ir on W(110). Many-atom effects are parametrized in terms of the trio interactions $F_{3\mathrm{lin}}$ in linear and $F_{3\mathrm{tri}}$ in triangular configurations. It is found that many-atom effects, rather than amounting to small perturbations of the pair contributions, are the *major* contributors to the cohesion of two-dimensional clusters for both Pd and Ir on W(110). [S0163-1829(99)08131-X]

I. INTRODUCTION

Interactions between adsorbed atoms play an important part in a variety of surface processes, among them diffusion, desorption, and the nucleation of new surface layers. Still not clear is the nature of adatom interactions in the cohesion of surface layers. The theory underlying such interactions is difficult and not yet quantitative enough to be applied to real systems.[1] Experimental efforts[2–8] interpreting phase diagrams or desorption phenomena have had to proceed indirectly, so that at the moment, relatively little is known about pair interactions between adatoms, and much less about many-atom contributions to cohesion.

Fortunately, the ability to see individual adatoms on a surface with the field ion microscope makes it possible to map out in some detail interactions between metal adatoms.[9] For pairs of adatoms, this is a straightforward matter. In a system at equilibrium with the underlying surface at a constant temperature T, the probability $P(\mathbf{R})$ of finding two adatoms a vector separation $\mathbf{R}$ apart is just[10]

$$P(\mathbf{R})=CP_0(\mathbf{R})\exp[-F(\mathbf{R})/kT]. \tag{1}$$

Here $F(\mathbf{R})$ is the free energy of interaction between the adatoms, $P_0(\mathbf{R})$ gives the number of ways the vector $\mathbf{R}$ can be accommodated on the surface, k is Boltzmann's constant, and C provides normalization. The probability $P(\mathbf{R})$ can be measured by counting the frequency $N(\mathbf{R})$ with which two adatoms are observed at a separation $\mathbf{R}$ in a canonical ensemble; the free energy of interaction for two atoms at different pairs of sites is therefore directly accessible.

For pairs of chemically identical atoms, quantitative measurements using the field ion microscope are available for Ir as well as for Re on the (110) plane of W and provide some insights into the important interactions on this densely packed plane.[11] These two atoms behave quite differently: Ir atoms in nearest-neighbor sites along $[1\bar{1}\bar{1}]$ attract each other, Re atoms suffer repulsion at small separations. For both, however, the free energy of interaction is significant over quite a considerable range, greater than 13 Å, and oscillates with distance along the close-packed direction $[1\bar{1}\bar{1}]$.

To what extent are these features characteristic of metal atoms in general? Are there obvious trends in pair interactions as the chemical identity of the atoms is changed? There remains an even more important question: do pair interactions really play a significant role in the stability of atomic clusters on a surface, or do many-atom effects dominate cohesion? As a start in probing these matters, we have examined the behavior of Pd atoms on W(110). Pd is an element in the same platinum family as Ir, which has already been explored,[11] but with a much lower binding energy to the W(110) surface.[2]

In Sec. II we outline the conditions under which the spatial distribution of two Pd atoms has been measured on W(110). The results of the observations, as well as the free energies of pair interactions derived from them, are presented in Sec. III. Comparisons with previous measurements of interactions reveal striking similarities with the behavior of Ir adatoms. We then make use of the quantitative data on pair interactions to probe the contributions of many-atom effects to cohesion. This is done in the final and most important section of this paper, where we examine the stability and shape of platinum metal clusters on W(110). Analyses of the transformations between differently shaped clusters provide detailed insights and allow us to evaluate the magnitude of many-atom interactions. This extensive examination demonstrates that many-atom effects contribute *decisively* to the stability of surface clusters.

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II. EXPERIMENTAL CONSIDERATIONS

We have used a helium-cooled field ion microscope[12] to locate individual adatoms on a W(110) surface and to measure adatom interactions. The techniques for determining pair interactions have previously been described in detail,[10] but some specifics are relevant here. Measurements have all been done on (110) planes, with ~ 22 lattice spacings along the [001] and $[1\bar{1}0]$ directions, created by field evaporation of single crystal tungsten wire (from Field Electron and Ion Sources Co., McMinnville, Oregon); during the course of the experiments, with continued field evaporation, the dimensions vary by ~ 2 lattice spacings. To establish a reliable distance scale, the sites at which Pd atoms are bound were mapped out by recording the location of a single atom in repeated diffusion intervals; this was done immediately following observations of the distribution of two adatoms over the (110) plane.

The temperature at which pair interactions are measured is a compromise. To ensure proper equilibration, it is desirable that the root-mean-square displacement during an equilibration interval amounts to at least ~ 1/5 of the diameter of the surface.[10] However, keeping the temperature low is advantageous, as the statistical uncertainty in the free energy of interaction is given by

$$\sigma[F(\mathbf{R})]=kT[\{1-P(\mathbf{R})\}/N(\mathbf{R})]^{1/2}. \tag{2}$$

Still, the temperature cannot be set too low, otherwise once a strongly attractive configuration forms, it will remain in place too long. Based on preliminary experiments, a temperature of 242 K was chosen as optimal for observations of Pd pairs.

A crucial factor in this choice is the behavior of Pd at the edges of the W(110) plane. During the extensive equilibration of an adatom pair, one or both of the atoms may wander away from the center of the (110) plane and occasionally reach the outer edge. If the atom then escapes, or becomes permanently bound to the edge, a new atom has to be deposited, quite a time consuming procedure. At temperatures in the vicinity of 242 K, a Pd atom bounces back from the edge to the center region without escaping from the top terrace of the W(110) plane, so that experiments to explore the various configurations on the surface can continue unimpeded.

In practice, two hours following deposition, after ~ 100 observations of various pair configurations have been made, the two adatoms as well as one or two layers of the surface are removed by field evaporation to eliminate any impurities that could have accumulated. Experiments are then continued with newly deposited adatoms.

Atoms that come close to the plane edge during equilibration may be subject to interactions atypical of the perfect (110) plane. In evaluating the data for use in estimating the free energy of interaction, observations in which one or both atoms are within three to four spacings from the edge are therefore rejected. During imaging, the electric field at the plane edges is higher than in the center. When an atom is detected near the plane edge after equilibration, the imaging voltage is therefore immediately lowered to avoid field evaporation of the atom.

To obtain reasonable estimates of the free energy $F(\mathbf{R})$ with a statistical uncertainty of ~ $kT/3$, roughly ten observations are desirable for each separation; in our case this implies a total of ~2000 observations. Once these are available, interactions can be derived by casting Eq. (1) in the form

$$F(\mathbf{R})/kT=C_\infty-\ln[N(\mathbf{R})/N_0(\mathbf{R})]. \tag{3}$$

Here, $N_0(\mathbf{R})$ is an entirely geometrical quantity, the number of observations for noninteracting atoms at a separation $\mathbf{R}$. It is obtained by direct counting of the separations accessible in the inner (perfect) region of the (110) plane. Normalization is achieved by setting a separation R_∞ beyond which interactions are negligible; the normalization constant C_∞ is then obtained from the requirement

$$C_\infty=\ln\left[\sum_{|\mathbf{R}|>R_\infty} N(\mathbf{R}) \Big/ \sum_{|\mathbf{R}|>R_\infty} N_0(\mathbf{R})\right]. \tag{4}$$

Finally, from Eqs. (3) and (4), observations of the number of pairs $N(\mathbf{R})$ at the separation $\mathbf{R}$ yield the desired quantity, the free energy of interaction $F(\mathbf{R})$ for two adatoms on the surface.

III. ADATOM PAIR INTERACTIONS

A. Results for Pd atoms

In experiments with two Pd atoms on W(110), the surface was equilibrated by warming to 242 K for 10 sec. Of 2151 observations on pairs, 1855 were found with both atoms in the inner region, sufficiently far from the edges, and were therefore accepted for analysis. The distribution of pairs over different separations is given in Table I; a plot of the results is shown in Fig. 1 out to a distance of $10a_0/2$, where a_0 is the lattice constant of W. As in previous studies,[10,11] relative separations have been mapped into the first quadrant, with one atom always set at the coordinates (0,0). For reasons of symmetry, the numbers in Fig. 1 have been displayed doubled along the axes [001] and $[1\bar{1}0]$, as there each point represents only two displacements, rather than four elsewhere. By far the largest number of observations is for atoms at the nearest-neighbor separation ℓ, that is at (1,1). In contrast, hardly any atoms are found in positions nearby, such as (2,0), (0,2), (3,1), and (1,3). Along the close-packed direction $[1\bar{1}1]$, the number of observations appears to oscillate with distance: after the peak at (1,1), only 3 are found at (2,2), but the number of pairs then rises again significantly to 16 at (3,3). Very few pairs are found along the [001] and $[1\bar{1}0]$ directions.

Free energies of interaction $F(\mathbf{R})$ have been derived in accordance with Eq. (3) and Eq. (4) from the data for the number of pairs $N(\mathbf{R})$ at a separation $\mathbf{R}$, compared to the number $N_0(\mathbf{R})$ expected in the absence of interactions. The results are summarized in Table II. At $\mathbf{R}=(0,2)$ and (3,1) no pairs were found. A lower bound to the free energy of interaction at these positions is obtained by assuming $N(\mathbf{R})\sim 1$. The cutoff distance which enters in evaluating the normalization constant C_∞ in Eq. (4) was set at $R_\infty=20a_0/2$. A trial value of R_∞ was picked first, based on a qualitative evaluation of how the distribution varied with interatomic separation. This choice was refined by establishing that the free

TABLE I. Number of observations $N(\mathbf{R})$ of Pd pairs on W(110) at the separation $\mathbf{R}$ after equilibration at 242 K.

Pd-Pd
T = 242 K

$a_o/\sqrt{2}$ → $[1\bar{1}0]$

y/x	0		2		4		6		8		10		12		$a_o/2$ → [001]		
	2		4														
		8		3		10		7		1							
	3		6		7		3		5		4		2				
		8		6		7		5		7		4		6			
	8		12		6		13		11		5		1		4		
		11		9		8		4		4		4		4		6	
8	4		4		8		5		8		4		12		2		
		8		8		5		5		9		3		9		6	
6	4		13		11		8		8		7		7		4		6
		9		8		14		8		6		5		11		5	
4	2		9		20		10		10		2		8		6		13
		1		16		17		12		7		6		3		5	
2	0		3		10		10		5		6		3		9		2
		562		0		15		10		9		6		4		4	
0	Pd		2		1		1		2		2		4		2		2

energies calculated from Eq. (3) and Eq. (4) no longer varied significantly with the particular value of R_∞.

The plot of free energies, in Fig. 2, makes it clear that interactions are highly anisotropic, repulsive along the [001] and $[1\bar{1}0]$ directions, and generally attractive along $[1\bar{1}1]$. At the nearest-neighbor separation (1,1), the interactions are most attractive and the free energy is -88.6 ± 0.7 meV. However, at separations in close proximity to this, such as (2,2), (3,1), and (1,3), interactions are clearly repulsive. Farther away, interactions tend to become attractive again. This trend is most apparent along $[1\bar{1}1]$, and is displayed in Fig. 3. Attractive interactions at separations $|\mathbf{R}|\geq 3$ nearest-neighbor spacings ℓ are separated from the very strong attractions at 1ℓ by repulsion at $|\mathbf{R}|=2\ell$.[13]

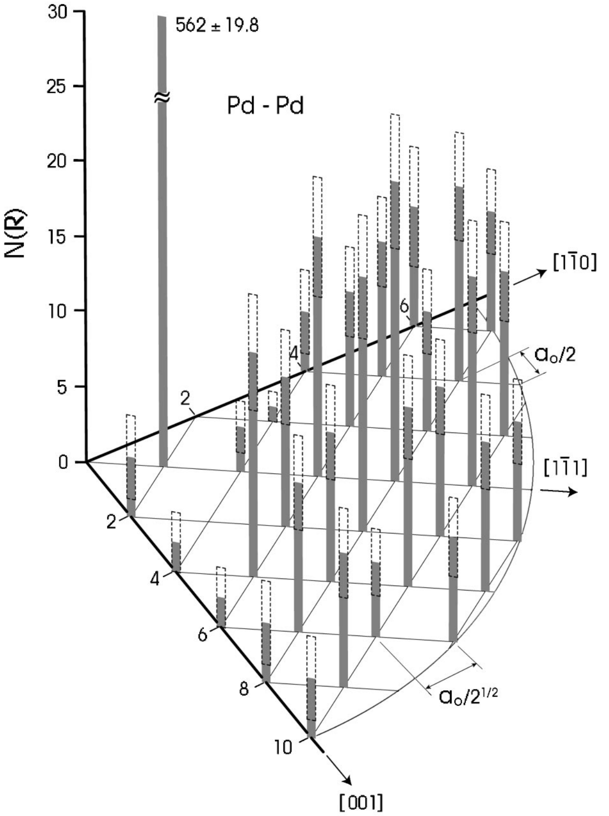

FIG. 1. Number of observations $N(\mathbf{R})$ of Pd pairs on W(110) at the separation $\mathbf{R}$, for $|\mathbf{R}|\leq 10a_0/2$. Pd atoms were equilibrated at 242 K for 10 sec. All observations are mapped into first quadrant, but along the two axes [001] and $[1\bar{1}0]$, $N(\mathbf{R})$ is displayed doubled to compensate for the fact that a vector *inside* the first quadrant represents four displacements, whereas *on* the axis a vector represents only two.

B. Comparisons

The interactions between two Pd atoms revealed in these plots are quite similar to what has been observed for Ir atoms on W(110).[11] To facilitate comparisons, structural and energy parameters for Pd and Ir are listed in Table III. How much alike interactions really are for Pd and Ir is clear in Fig. 4(a), showing the free energies for both along the close-packed direction $[1\bar{1}1]$. At the nearest-neighbor separation ℓ, interactions between Pd and Ir atoms are the same within a standard deviation,[14] and they are not too far apart elsewhere beyond $|\mathbf{R}|>\ell$. Pair interactions between two Re atoms[11] are compared with those for Pd in Fig. 4(b). At longer separations, interactions between Re atoms along $[1\bar{1}1]$ are little different from those in Pd pairs, even though Re atoms at (1,1) as well as (2,2) are strongly repelled by a Re atom at (0,0). Bauer[15] has suggested a correlation between pair interactions and the strength of atom binding to the surface. However, the cohesive energy of Ir is 1.76 times as great as that of Pd, and the desorption energies of Ir and Pd from W(110) stand in the ratio 2.13:1;[2] despite that, the free energies of interaction are almost the same. There is clearly more to be done here.

It is important to note that these pair energies, obtained from direct observations of two atoms on a W(110) plane, differ in magnitude from estimates for related platinum metals obtained indirectly from macroscopic measurements of desorption by Kolaczkiewicz and Bauer.[2] For rhodium, they deduce a nearest-neighbor pair interaction of 0.6 eV, for platinum it amounts to 0.8 eV. These estimates are an order of magnitude larger than what we find for Pd or Ir on the same surface. Although detailed comparisons are not yet possible, it would appear that these indirect methods have not yet succeeded in isolating interactions with just one other adatom.

IV. MANY-ATOM INTERACTIONS

With information about pair interactions between metal adatoms now available, it is straightforward to evaluate pair contributions to the cohesion of surface layers. For the first time we are therefore in a position to also get a quantitative idea of the role of many-atom effects. That many-atom interactions must be considered in estimating the energetics of overlayers is generally recognized, but it is still not clear how strong these interactions really are and how significantly they contribute to the cohesion of clusters and overlayers.

In the past, efforts to quantitatively establish these contributions have usually involved taking a few near-neighbor interactions together with some many-atom effects as parameters, and then varying these parameters to fit information from macroscopic experiments.[2–8] However, this approach does not uniquely define interaction parameters.[16,17] For metal layers, it also ignores the fact that pair interactions are

TABLE II. $F(\mathbf{R})$, the free energy of interaction for Pd pairs on W(110), equilibrated at 242 K.

Pd-Pd
T = 242K

$a_o/\sqrt{2}$ → [$\bar{1}$10]

y / x	0		2		4		6		8		10		12		14		
	1.9±14.7		1.6±10.4														
		−11.4±7.4		8.7±12.0		−17.2±6.6		−10.8±7.9		28.3±20.9							
	−4.1±12.0		−4.3±8.5		−8.2±7.9		8.7±12.0		−3.3±9.3		−0.5±10.4		12.1±14.7				
		−9.0±7.4		−3.5±8.5		−7.4±7.9		−1.6±9.3		−10.1±7.9		−0.3±10.4		−11.0±8.5			
10	−22.3±7.4		−16.6±6.0		−2.7±8.5		−19.8±5.8		−17.7±6.3		−3.0±9.3		28.5±20.9		−2.8±10.4		
		−13.5±6.3		−9.8±6.9		−8.2±7.4		5.1±10.4		3.4±10.4		1.6±10.4		−0.6±10.4		−11.6±8.5	
8	−5.7±10.4		8.5±10.4		−6.8±7.4		2.0±9.3		−9.3±7.4		3.4±10.4		−21.6±6.0		13.5±14.7		
		−4.9±7.4		−5.4±7.4		3.5±9.3		2.1±9.3		−11.8±6.9		9.1±12.0		−16.0±6.9		−10.2±8.5	
6	−3.8±10.4		−14.3±5.8		−11.6±6.3		−6.2±7.4		−7.8±7.4		−6.9±7.9		−9.0±7.9		0.1±10.4		−11.0±8.5
		−5.5±6.9		−3.7±7.4		−16.4±5.6		−6.3±7.4		−2.2±8.5		−0.4±9.3		−19.2±6.3		−5.3±9.3	
4	12.4±14.7		−5.0±6.9		−22.6±4.6		−9.6±6.6		−11.4±6.6		20.2±14.7		−11.0±7.4		−7.4±8.5		−26.2±5.8
		42.0±20.9		−16.7±5.2		−19.4±5.0		−13.9±6.0		−4.5±7.9		−3.5±8.5		8.7±12.0		−4.6±9.3	
2	>(28.5±20.9)		19.4±12.0		−7.2±6.6		−8.8±6.6		3.8±9.3		−2.1±8.5		10.1±12.0		−15.3±6.9		13.3±14.7
		−88.6±0.7		>(42.0±20.9)		−16.1±5.4		−9.5±6.6		−9.3±6.9		−3.0±8.5		3.1±10.4		0.4±10.4	
0	Pd		14.0±14.7		26.8±20.9		25.1±20.9		8.7±14.7		6.7±14.7		−10.1±10.4		1.9±14.7		−0.9±14.7

$a_o/2$ → [001]

important over considerable distances, and are not adequately described by near-neighbor energies alone.[9] At the moment, it is not even certain whether many-atom contributions to cohesion in metal layers are attractive or repulsive.[9,18]

In principle, interactions between more than two atoms can be measured directly, by relying on an extension of Eq. (1) used to describe adatom pairs. For three atoms, the free energy of interaction $F(\mathbf{R}_{12},\mathbf{R}_{23})$ can be obtained by measuring the probability $P(\mathbf{R}_{12},\mathbf{R}_{23})$ of finding the atoms at the relative separations $\mathbf{R}_{12}$ and $\mathbf{R}_{23}$ from each other, using the relation

$$P(\mathbf{R}_{12},\mathbf{R}_{23})=CP_0(\mathbf{R}_{12},\mathbf{R}_{23})\exp[-F(\mathbf{R}_{12},\mathbf{R}_{23})/kT]; \tag{5}$$

here $P_0(\mathbf{R}_{12},\mathbf{R}_{23})$ gives the number of ways the vectors $\mathbf{R}_{12}$ and $\mathbf{R}_{23}$ can be accommodated on the surface. In practice, however, amassing the statistics necessary for reliable energies has so far proved too daunting a task to implement this approach.

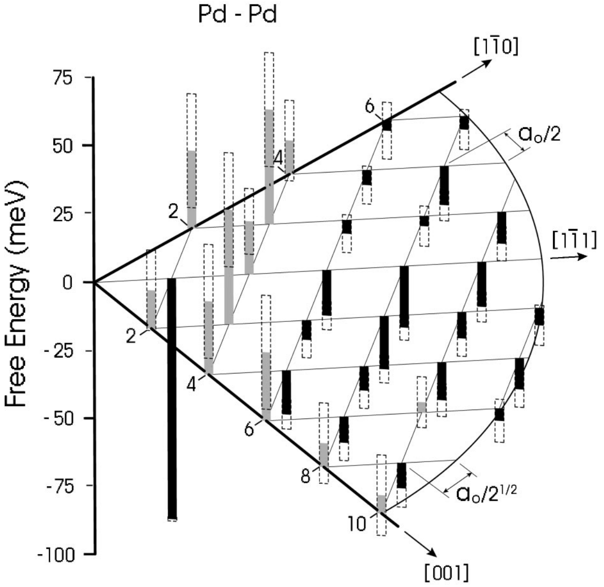

FIG. 2. Free energy of interaction $F(\mathbf{R})$ for Pd pairs on W(110), equilibrated at 242 K. Values derived from data in Table I, using Eqs. (3) and (4). Repulsive interactions in gray, attractive in black. For the separation $\mathbf{R}=(0,2)$ and $\mathbf{R}=(3,1)$, the free energies and their statistical scatter are estimated lower bounds.

Nevertheless, there are indications from dissociation measurements of stable trimers that the many-atom effect can be significant. For Re atoms on W(110), Fink[19,20] demonstrated that although pair interactions between two Re atoms are repulsive, trio effects, that is contributions to the total interactions from three atoms, above and beyond effects from pairs, provide sufficient bonding to make the trimer thermo-

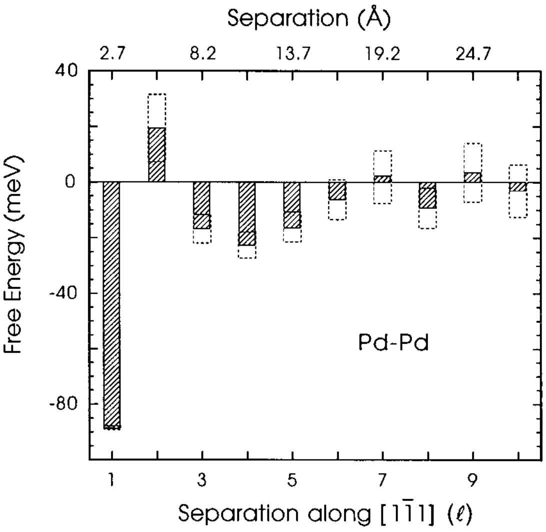

FIG. 3. Free energy of interactions for Pd pairs along the [$1\bar{1}1$] direction. Separation along [$1\bar{1}1$] in units of the nearest-neighbor distance $\ell=(3^{1/2}/2)a_0$, where a_0 is the lattice constant of W.

TABLE III. Structural and energy parameters for Pd and Ir.

	Pd	Ir
Nearest-neighbor Distance for bulk solid (Å)[a]	2.7509	2.7147
Bulk Modulus (10^{11} N/m^2)[b]	1.808	3.55
Crystal Structure	fcc	fcc
Atomic Electronic Structure	(Kr)$(4D)^{10}$	(Xe)$(6S)^2(4F)^{14}(5D)^7$
Desorption Energy from W(110) (eV/atom)[c]	3.2	6.8
Cohesive Energy (eV/atom)[a]	3.92	6.90
Melting Point (K)[a]	1828	2719
Free Energy for Nearest Pair (meV)	−88.6±0.7	−86.0±2.0[d]

[a] Reference 32.
[b] Reference 33.
[c] Reference 2.
[d] Reference 11.

dynamically stable. Trio effects also seem to contribute, if less dramatically, to the cohesion of Ir_3 on W(110).[11]

How significant are many-atom interactions to the cohesion of clusters in general? How important are they compared to pair contributions for clusters on W(110)? In order to examine this question, we draw upon the observation that platinum-family atoms tend to form chains with a spacing identical to that of the lattice along $[1\bar{1}1]$ when equilibrated on W(110).[21–26] As the number of atoms in a chain increases over a certain critical size, the linear structures transform into a more compact shape pseudomorphic with the substrate.[23–26] Structural changes in surface layers when the concentration is increased have in the past been used in attempts to estimate interactions between adatoms of electronegative gases, but with uncertain success.[16] With direct measurements of pair interactions in hand, however, we are in a much sounder position to examine the role of many-atom interactions in the stability of metal clusters on W(110).

A. Pd on W(110)

1. Qualitative considerations

For palladium, Bassett[23] reported that clusters containing as many as eight atoms formed chains, but that clusters of ten or more atoms were more stable as compact two-dimensional (2D) clusters; later, chains of nine Pd atoms were found to be metastable.[24] For Pd_8, the structural rearrangements from linear to compact clusters are reversible, as is evident in Fig. 5; after equilibration at 242 K, this cluster can exist either in a linear or compact form. Once one Pd atom is field evaporated and Pd_7 is formed, equilibration at 242 K never produces the island configuration: the cluster remains in the linear configuration. For clusters of seven or fewer atoms, only linear chains are observed at 242 K. On the contrary, when there are 9 or more Pd atoms in a cluster, only the island form is observed at equilibrium. Long metastable chains, containing more than eight Pd atoms, can be grown from Pd_7 by adding Pd atoms one by one at 210 K (Fig. 6). However, on equilibration at 242 K, these chains change irreversibly to a more compact 2D arrangement.

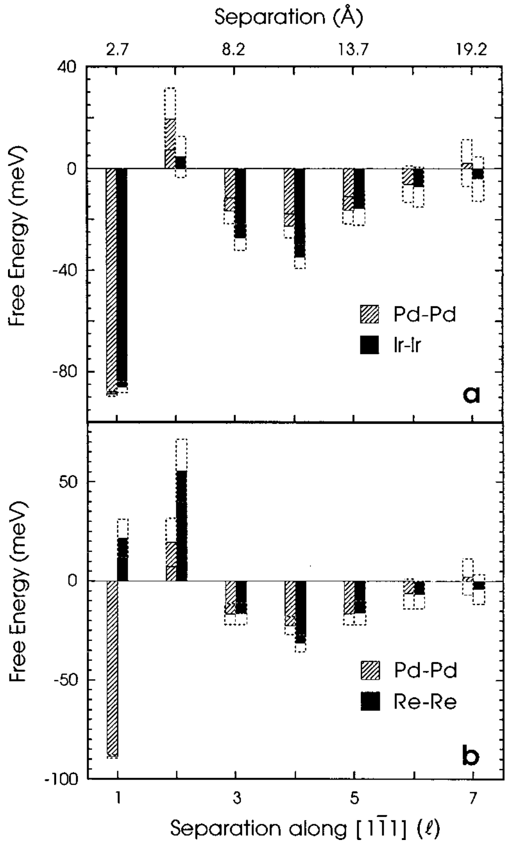

FIG. 4. Free energies of pairs along $[1\bar{1}1]$ of W(110). (a) Interactions for Pd and Ir pairs are almost the same within the statistical scatter. (b) Comparison of free energy for Pd and Re pairs. Beyond 2ℓ, interactions are almost the same within the statistical scatter. Data for Ir and Re are from Ref. 11.

Do pair interactions between Pd atoms correctly predict these changes in cluster structure? In Fig. 7 are plotted the pair contributions to the free energies of Pd clusters of increasing size when in a linear as compared to a two-dimensional arrangement. Many different forms are possible in the latter; for this comparison we have picked the physically reasonable arrangements shown in the figure. Linear and triangular trimers are very close in energy, but for Pd_4 the island configuration appears to be favored over the chains, which are the ones actually observed. Thereafter the linear chain is always the configuration with the lower pair energy; as the cluster size increases, the difference in pair energies between islands and chains becomes ever larger. That, of course, is just as expected from the fact that pair interactions are attractive along the $[1\bar{1}1]$ direction, along which the chains are oriented, but repulsive along the orthogonal directions [001] and $[1\bar{1}0]$. To build a 2D cluster, pairs must be put in the latter, unfavorable positions. Relying on pair interactions only, we therefore *cannot* account for the fact that islands and chains of eight atoms are actually of comparable stability, and that for clusters larger than that the

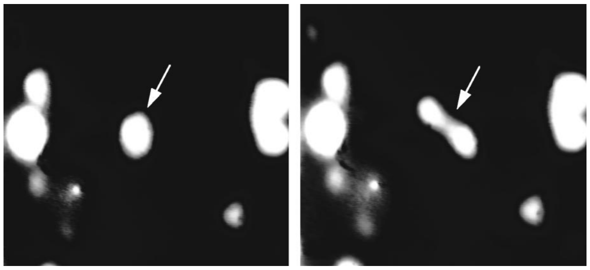

FIG. 5. Field ion microscope images, showing equilibration of Pd_8 (marked by arrow) in center of W(110) at 242 K. Two-dimensional island configuration at left is reversibly transformed into chain at right by heating.

island configuration is preferred. Significant many-atom interactions must be invoked to account for the linear structure actually observed for clusters from Pd_3 to Pd_7, and for the stability of 2D islands of nine or more Pd atoms.

2. Quantitative analysis

A more quantitative idea of many-atom effects is easily obtained for trimers, different configurations of which, denoted as linear, triangular, and bent, are shown in Fig. 8. The free energies of trio interactions in these configurations will be denoted by $F_{3\mathrm{lin}}$, $F_{3\mathrm{tri}}$, and $F_{3\mathrm{bent}}$, and the total free energy of interactions for these configurations can now be written as

$$F_{\mathrm{lin}}=2F(1,1)+F(2,2)+F_{3\mathrm{lin}},$$

$$F_{\mathrm{tri}}=2F(1,1)+F(2,0)+F_{3\mathrm{tri}},$$

$$F_{\mathrm{bent}}=2F(1,1)+F(0,2)+F_{3\mathrm{bent}}, \tag{6}$$

where $F(a,b)$ is the measured free energy of a pair at the separation $\mathbf{R}=(a,b)$. The trimer is always found in the form of a linear chain. To account for this fact we must satisfy the relation

$$P_{\mathrm{lin}}>P_{\mathrm{tri}}+P_{\mathrm{bent}}. \tag{7}$$

The probability of observing a particular form, say P_{bent}, depends exponentially upon the free energy through

$$P_{\mathrm{bent}}=C\Omega_{\mathrm{bent}}\exp[-F_{\mathrm{bent}}/kT], \tag{8}$$

where Ω_{bent} gives the number of energetically equivalent configurations with bent shape, and C is just a normalization constant. Inasmuch as the pair free energies $F(a,b)$ in Eq. (6) are known, Eqs. (7) and (8) in effect constrain the trio interactions $F_{3\mathrm{lin}}$, $F_{3\mathrm{tri}}$, and $F_{3\mathrm{bent}}$ to a limited range of allowed values through the requirement[27]

$$\begin{aligned}&\Omega_{\mathrm{lin}}\exp[-\{2F(1,1)+F(2,2)+F_{3\mathrm{lin}}\}/kT]\\&\quad>\Omega_{\mathrm{tri}}\exp[-\{2F(1,1)+F(2,0)+F_{3\mathrm{tri}}\}/kT]\\&\qquad+\Omega_{\mathrm{bent}}\exp[-\{2F(1,1)+F(0,2)+F_{3\mathrm{bent}}\}/kT].\end{aligned} \tag{9}$$

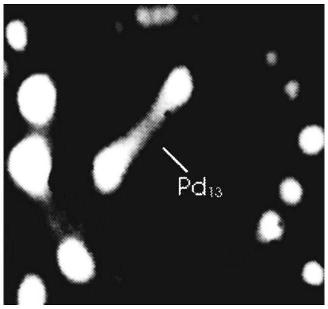

FIG. 6. Metastable linear chain of Pd_{13}, grown on W(110) from Pd_7 by addition of one Pd atom at a time at 210 K. On warming at 242 K, chain converts irreversibly to island.

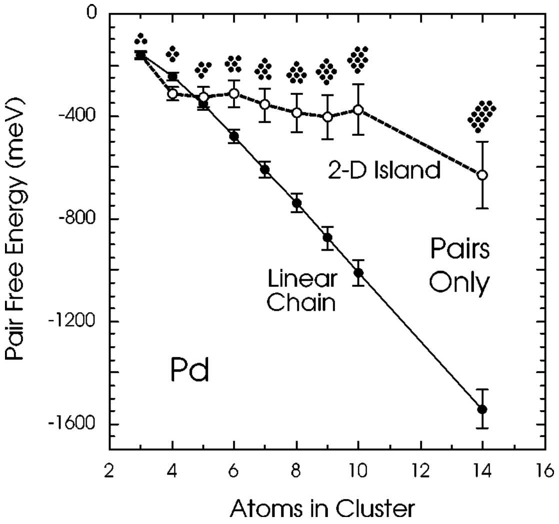

FIG. 7. Free energy of linear Pd clusters and illustrated island shapes on W(110) at 242 K, calculated from data in Table I assuming only pair interactions.

The same procedure can be applied to tetramers, although for them, in the forms *A, B, C, D,* and *L* in Fig. 9, we should in principle also entertain possible contributions from quarto effects, that is from contributions of four atoms at a time beyond those from pairs and trios. We will, however, ignore

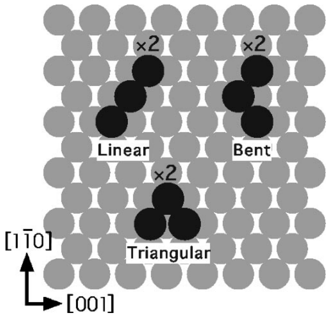

FIG. 8. Schematics of different trimer configurations on W(110), showing the degeneracy of linear, bent, and triangular forms.

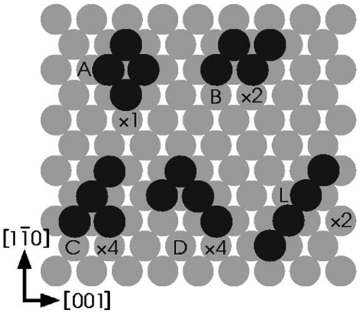

FIG. 9. Tetramer forms and their degeneracies on W(110).

these henceforth, and write the free energies of interaction for the forms *A, B, C, D*, and *L* as

$$F_A = 4F(1,1) + F(0,2) + F(2,0) + 2F_{3\mathrm{tri}} + 2F_{3\mathrm{bent}},$$

$$F_B = 3F(1,1) + 2F(2,0) + F(3,1) + 2F_{3\mathrm{tri}},$$

$$F_C = 3F(1,1) + F(2,2) + F(0,2) + F(2,0) + F_{3\mathrm{lin}} + F_{3\mathrm{tri}} + F_{3\mathrm{bent}},$$

$$F_D = 3F(1,1) + F(2,2) + F(2,0) + F(3,1) + F_{3\mathrm{lin}} + F_{3\mathrm{tri}},$$

$$F_L = 3F(1,1) + 2F(2,2) + F(3,3) + 2F_{3\mathrm{lin}}. \tag{10}$$

Inasmuch as the linear form *L* has been found to predominate, we impose the requirement that

$$P_L > P_A + P_B + P_C + P_D. \tag{11}$$

This establishes another constraint to be met by the trio parameters $F_{3\mathrm{lin}}$, $F_{3\mathrm{tri}}$, and $F_{3\mathrm{bent}}$.

The same approach applied to larger clusters serves to more closely confine values of the three trio energies. The relative stabilities observed for clusters containing from three to ten as well as 14 atoms restrict the allowed values to a small region, plotted in Fig. 10. $F_{3\mathrm{lin}}$ must be attractive, with a magnitude of ∼ 60 meV or larger, that is comparable with the strongest pair interaction of −88.6 meV. For a fixed value of $F_{3\mathrm{lin}}$, the allowed values of $F_{3\mathrm{tri}}$ and $F_{3\mathrm{bent}}$ fall into narrow strips, five of which are shown in Fig. 10. For any one strip, the free energy of cohesion turns out to be roughly constant, and not sensitively dependent upon the particular values of $F_{3\mathrm{tri}}$ and $F_{3\mathrm{bent}}$. To simplify the presentation of results, the trio energies $F_{3\mathrm{tri}}$ in the triangular configuration and $F_{3\mathrm{bent}}$ in the bent configuration are set equal to each other, so they fall on the hatched plane in Fig. 10. Many-atom effects can now be expressed entirely in terms of the two parameters, $F_{3\mathrm{lin}}$ and $F_{3\mathrm{tri}}$, giving the contributions of the linear and nonlinear trio configurations. The allowed values of these two parameters fall into a very narrow needle-shaped region, shown in white in Fig. 11; the darkly shaded regions are excluded by the stability conditions for one or another Pd cluster, as indicated.

It appears from Fig. 11 that the smallest attractive contribution from the trio effects amounts to roughly −60 meV for $F_{3\mathrm{lin}}$ and −25 meV for $F_{3\mathrm{tri}}$, which can be safely regarded as true upper bounds. $F_{3\mathrm{lin}}$ especially could be significantly more attractive, considerably exceeding even the strongest pair interactions. However, allowed values of the parameter $F_{3\mathrm{tri}}$ depend only weakly on the magnitude of $F_{3\mathrm{lin}}$. The significance of these trio interaction energies for the cohesion of clusters will be considered later, but it is already clear that these are important effects.

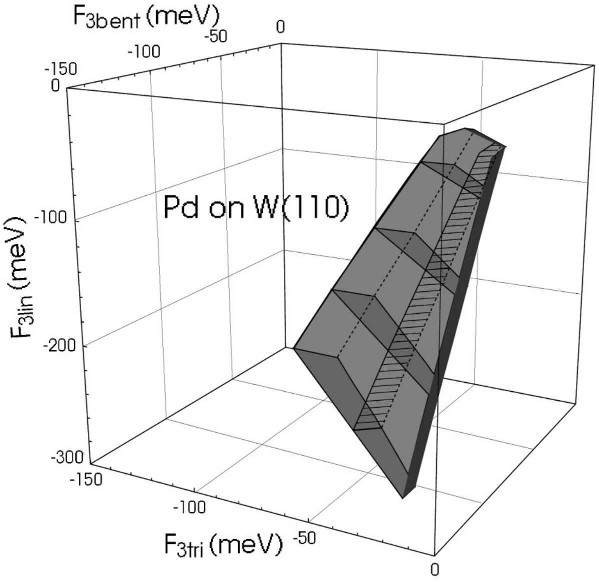

FIG. 10. Allowed values of $F_{3\mathrm{tri}}$, $F_{3\mathrm{bent}}$, and $F_{3\mathrm{lin}}$ for Pd on W(110) at 242 K. For each cluster size, inequalities like Eq. (9) confine the values of the three trio energies, leaving only the allowed volume shown in gray. Along the hatched surface, $F_{3\mathrm{tri}}$ equals $F_{3\mathrm{bent}}$. Allowed $F_{3\mathrm{tri}}$ and $F_{3\mathrm{bent}}$ are plotted at five values of $F_{3\mathrm{lin}}$ and appear as strips shown in darker gray.

B. Ir on W(110)

Ir atoms on W(110) also form chains along $[1\bar{1}1]$, but clusters containing 15 or more atoms are known to be thermodynamically preferred when in a compact, two-dimensional configuration.[25] Pair interactions have already been characterized in detail,[11] and in Fig. 12 the pair contributions to the free energies are shown for linear as well as island shaped clusters.[28] Just as for Pd clusters in the pair approximation, as the size increases, linear clusters become even more thermodynamically advantageous compared to two-dimensional islands, in gross contradiction to the observed behavior of Ir clusters.

For Ir, however, there is an additional effect. With pair interactions alone, larger island clusters (with more than 7 atoms, for example) are *unstable*: interactions are actually repulsive, that is, the free energies are positive. This comes about because for Ir atoms, the pair energies $F(2,0)$ and $F(0,2)$ are much more strongly repulsive than for Pd. Many-atom interactions evidently have to play a very important role in larger Ir clusters in order to compensate for the repulsive pair contributions and to bring the free energy of islands below the values for chains once the cluster has 15 atoms in it.

By following the procedures outlined in the preceding section, many-atom interactions can be defined in terms of the parameters $F_{3\mathrm{tri}}$, $F_{3\mathrm{bent}}$, and $F_{3\mathrm{lin}}$, to yield the map in Fig. 13, showing the allowed region in parameter space. For a given $F_{3\mathrm{lin}}$, allowed values of $F_{3\mathrm{tri}}$ and $F_{3\mathrm{bent}}$ again fall

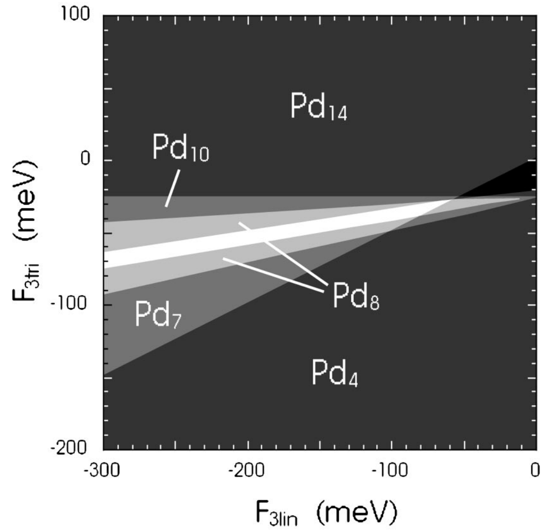

FIG. 11. Allowed values of $F_{3\text{lin}}$ and $F_{3\text{tri}}$ for Pd on W(110) at 242 K, based on the assumption $F_{3\text{tri}}=F_{3\text{bent}}$. For each size cluster, the stability conditions exclude part of the area, shown in gray. When all excluded regions are combined, only a needle-shaped, white allowed zone is left. For clarity, only five excluded areas are shown here.

into narrow strips, for which the total free energy of interaction is roughly constant. We therefore simplify matters by assuming $F_{3\text{tri}}\sim F_{3\text{bent}}$, and represent trio effects with just the two parameters $F_{3\text{lin}}$ and $F_{3\text{tri}}$. The plot of allowed trio parameters for Ir on W(110), in Fig. 14, is somewhat similar to that for Pd. It has a broader but still needlelike appearance, with allowed values for the trio interaction $F_{3\text{tri}}$ of much the same magnitude as for Pd; linear trio effects $F_{3\text{lin}}$ are much more negative, however. Obviously, trio effects contribute significantly to cohesion of Ir clusters also.

C. Comparisons

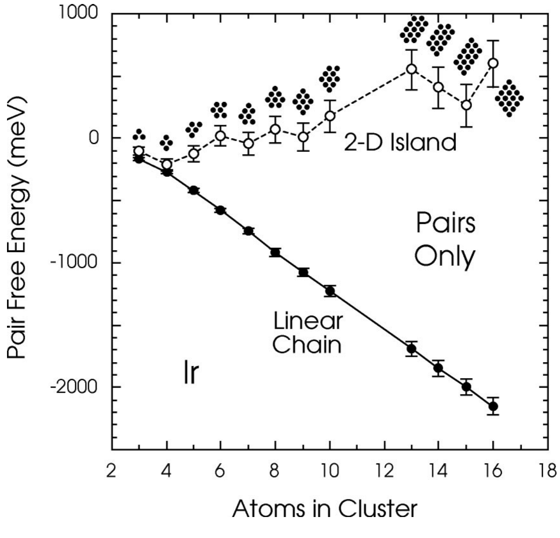

FIG. 12. Free energies of linear and illustrated island shapes of Ir clusters on W(110), assuming that only pair interactions contribute. For pair interactions from Ref. 11, only Ir chains are predicted to exist at equilibrium.

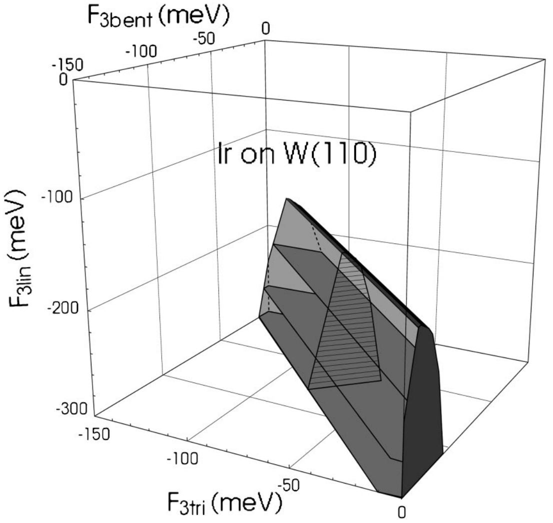

FIG. 13. Allowed values of $F_{3\text{tri}}$, $F_{3\text{bent}}$, and $F_{3\text{lin}}$ for Ir on W(110), shown in gray. For the hatched surface, $F_{3\text{tri}}$ equals $F_{3\text{bent}}$. Allowed $F_{3\text{tri}}$ and $F_{3\text{bent}}$ are indicated in darker gray at four fixed values of $F_{3\text{lin}}$.

To obtain a clearer appreciation for the contributions of many-atom effects to the cohesion of Pd and Ir clusters, the total free energy of interaction has been estimated for trio parameters close to the tip of the allowed parameter space in Figs. 11 and 14, that is under conditions where trio effects are minimal. The free energy of Pd clusters, estimated with pair interactions alone is compared in Fig. 15 with the free energy allowing for trio effects. A similar comparison is made in Fig. 16 for Ir clusters. For Pd chains, that is for clusters with less than eight atoms, many-atom interactions, indicated by the striated region between the two curves in Fig. 15, provide roughly as much cohesion as do pair interactions. For the smallest 2D Pd clusters (Pd_9), many-atom interactions contribute as much as $\sim\frac{2}{3}$ of the total cohesion. The fractional contribution becomes even larger as the size increases; for Pd_{14}, many-atom interactions amount to as much as $\sim\frac{3}{4}$ of the total. With iridium clusters, many-atom contributions are even more impressive. For Ir_3, roughly half the cohesion can be ascribed to trio effects, in good agreement with the dissociation experiments of Watanabe and Ehrlich.[11] For 2D Ir islands with 15 or more atoms, *all* of the cohesion arises from many-atom effects.

It must be emphasized that we have parametrized many-atom effects entirely in terms of the trio energies $F_{3\text{lin}}$ and $F_{3\text{tri}}$; both linear and triangular trio terms turn out to be attractive and provide binding comparable to that of nearest-neighbor pair interactions for Pd as well as Ir clusters on W(110). Although our neglect of quarto and higher effects is arbitrary, and done entirely for the sake of simplicity, that trio interactions are strongly attractive is well founded in direct observations. Previous studies on Ir trimers on W(110) (Ref. 11) already demonstrated that trio effects are in fact attractive and of the same order of magnitude as the strongest pair interactions; the trio energy $E_{3\text{lin}}$ for the linear configuration was estimated as -130 ± 70 meV, which falls inside of the allowed region of Fig. 14. Even more decisive are results for Re trimers on W(110).[11,19,20] The measured trio energy is much more attractive than for Ir. Allowing higher order interactions, such as quartos, in our comparisons could possibly lower our estimates for the strength of trio effects. It

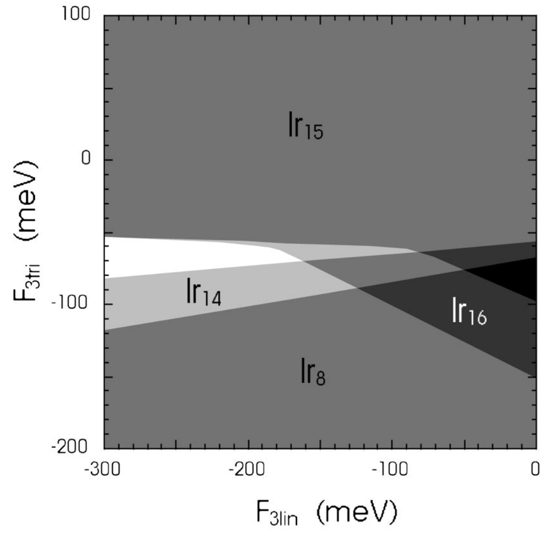

FIG. 14. Allowed values of $F_{3\mathrm{lin}}$ and $F_{3\mathrm{tri}}$ for Ir on W(110), based on the assumption $F_{3\mathrm{tri}}=F_{3\mathrm{bent}}$. For each size of cluster, the stability conditions exclude a region depicted in gray. When all excluded regions are combined, the needle-shaped zone in white is left. Only four excluded areas are shown here.

would not in any way alter the conclusion that many-atom interactions are strongly attractive and a major contributor to cohesion.

Calculations using embedded atom potentials have shown somewhat similar effects. For Pt, Pd, as well as Ni clusters on Pt(001), Wright *et al.*[29] found interactions between nearest neighbors attractive, but repulsive between second-nearest neighbors; trio effects were all attractive. From lattice gas simulations of the low-coverage portion of the phase boundary reported by Kolaczkiewicz and Bauer[30] for silver on W(110), Stoop[6] was able to derive approximate values for pair as well as trio interactions. He concluded that nearest-neighbor as well as trio interactions were attractive, 2nd as well as 3rd nearest neighbors were repulsive. Best agreement with experiments was found for $\varepsilon_1=-74$, $\varepsilon_2=\varepsilon_3=37$, $\varepsilon_4=\varepsilon_5=0$, $\varepsilon_{3\mathrm{tri}}=\varepsilon_{3\mathrm{bent}}=-37\,\mathrm{meV}$, where the ε_i's are pair energies for the ith nearest neighbor; $\varepsilon_{3\mathrm{tri}}$ and $\varepsilon_{3\mathrm{bent}}$ denote trio energies for the triangular and bent configurations, respectively. These results are generally similar to our findings for Pd on W(110), but Stoop ignored longer range interactions as well as linear trio effects, which we have found very important.

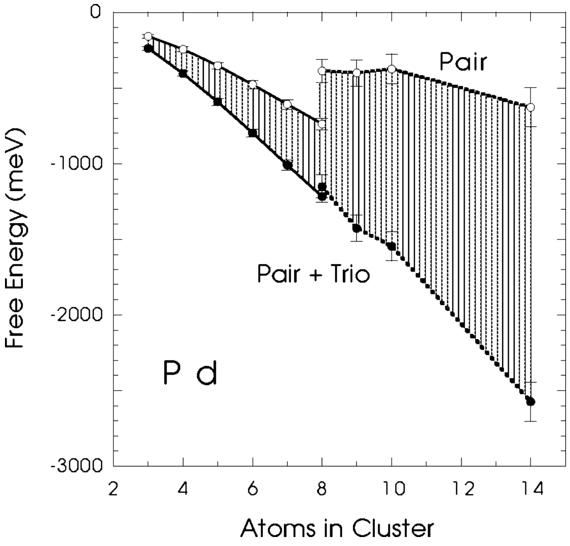

FIG. 15. Contribution of pair and trio interactions to the cohesion of Pd clusters on W(110) evaluated for $(F_{3\mathrm{lin}},F_{3\mathrm{tri}})=(-80\,\mathrm{meV},-34\,\mathrm{meV})$. Even for small linear chains (Pd_x, $x<8$), trio contributions to cohesion (shown striated) are comparable to pair effects. For islands (Pd_x, $x>8$), trio effects dominate cohesion. Free energy of 2D islands is shown dotted.

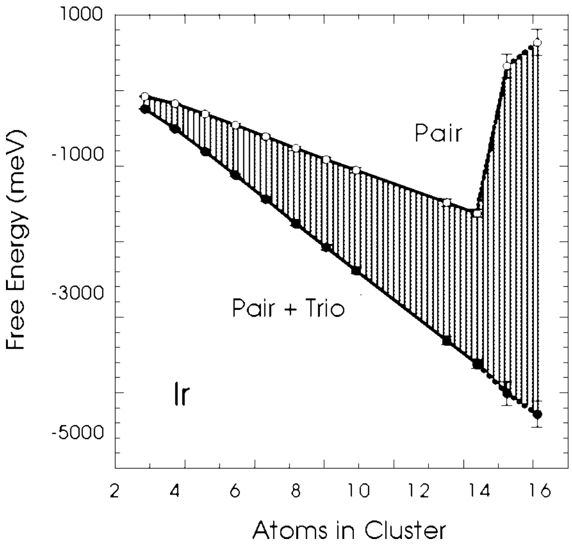

FIG. 16. Contribution of pair and trio interactions (the latter striated) to the cohesion of Ir clusters on W(110). Evaluated for $(F_{3\mathrm{lin}},F_{3\mathrm{tri}})=(-180\,\mathrm{meV},-68\,\mathrm{meV})$. For linear chains ($\mathrm{Ir}_x$, $x\leqslant 14$), trio interactions make roughly the same contribution to the cohesion as pair interactions. For islands (Ir_x, $x>14$), cohesion arises entirely from trio effects. Free energies of islands are shown dotted.

Somewhat later, however, Gollisch[31] made estimates of the cohesion of Cu and Au clusters on W(110), using an entirely empirical potential. From these estimates, Roelofs and Bellon[5] deduced that all pair interactions were attractive, but trio effects were repulsive. They gave the following values for Cu: $\varepsilon_1=-222$, $\varepsilon_2=-147$, $\varepsilon_3=-72$, $\varepsilon_{3\mathrm{tri}}=8$, and $\varepsilon_{3\mathrm{bent}}=52\,\mathrm{meV}$. Using these parameters, Roelofs and Bellon were not able to reproduce the phase boundaries reported by Kolaczkiewicz and Bauer,[30] but suggested that a proportionate lowering of both pair and trio effects could bring better agreement. For Au on W(110), the parameters extracted from Gollisch's estimates followed roughly the same pattern as for Cu: $\varepsilon_1=-293$, $\varepsilon_2=-255$, $\varepsilon_3=-146$, $\varepsilon_{3\mathrm{tri}}=23$, $\varepsilon_{3\mathrm{bent}}=158$, and $\varepsilon_{\mathrm{quarto}}=-148\,\mathrm{meV}$. Again there were significant discrepancies between the phase boundaries predicted from these parameters and actual observations, but Roelofs and Bellon implied that making quartos repulsive could improve agreement. We have to emphasize here that the choice of repulsive trios was made to conform with Gollisch's entirely empirical calculations, and not in response to any experimental information.

In continuing studies of rhodium and platinum adsorption on W(110), Kolaczkiewicz and Bauer[2] have recently derived interaction energies for a single atom in contact with one, two, and also three nearest-neighbor adatoms. From their results, one would have to conclude that the sum of trio effects plus second-neighbor interactions along $[1\bar{1}\bar{1}]$ are repulsive by 500 meV for Pt and by 200 meV for Rh. Their nearest-neighbor energies, however, are unusually large, 800 meV for Pt and 600 meV for Rh, which makes subsequent deductions uncertain.

The notion in some macroscopic studies that many-atom interactions are repulsive, and cohesion comes primarily from pair contributions, stems at least in part from a lack of detailed information about the strength of pair interactions. From direct measurements on Pd as well as Ir on W(110), we know that in 2D islands, strong attractions in nearest-neighbor pairs are counterbalanced by repulsions characteristic of 2nd and 3rd nearest neighbors. Overall, pair contributions in islands are therefore small. From our studies it emerges unequivocally that for Pd and even more so Ir clusters on W(110), many-atom effects rather than pair interactions are most important in affecting cohesion.

V. SUMMARY

We have been able to quantitatively characterize interactions between isolated adatoms. For Pd and Ir atoms on W(110), pair interactions are found to be similar. In addition to the features known from previous studies, such as the pronounced spatial anisotropy of interactions, their long (>13 Å) range, and the oscillatory dependence upon distance along the close-packed direction $[1\bar{1}\bar{1}]$, a surprising fact has emerged: at least for Pd and Ir, no pronounced dependence of pair interactions upon the binding energy of the individual atoms to the substrate has been found.

Truly quantitative determinations of many-atom effects are still lacking, but by taking advantage of the transformation from linear to two-dimensional clusters characteristic of the platinum metals on W(110), it has been possible to map out regions of allowed values for trio interactions. Many-atom interactions are found to be strongly attractive and to dominate the thermodynamic properties of larger clusters. Such effects clearly have to be reckoned with in attempts to model cluster properties, but it will also be important to establish whether these trends extend to other surfaces.

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